



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/GB88/00117 (22) International Filing Date: 23 February 1988 (23.02.88) (31) Priority Application Number: 8704142 (32) Priority Date: 23 February 1987 (23.02.87) (33) Priority Country: GB (71) Applicant (for all designated States except US): WHITFORD PLASTICS LIMITED [GB/GB]; Brindley 86, Astmoor, Runcorn, Cheshire WA7 1PF (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : PORTER, Christopher, Scott [GB/GB]; 101 Brookhurst Avenue, Bromborough, Merseyside (GB). POWELL, John [GB/GB]; Whitford Plastics Ltd., Brindley 86, Astmoor, Runcorn, Cheshire WA7 1PF (GB).		(74) Agent: CLIFFORD, Frederick, Alan; Marks & Clerk, 57-60 Lincoln's Inn Fields, London WC2A 3LS (GB). (81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: PROTECTIVE SURFACE TREATMENT			
(57) Abstract <p>To a first organic liquid which has dissolved therein a fluorocarbon polymer e.g. 5 to 50% w/w e.g. PVDF, is added a second, compatible, non-solvent organic liquid in an amount (e.g. 1-50%) w/w such as to leave the polymer in solution. The mixed solution is applied to a structural, leatherlike or (especially) fabric substrate and heated e.g. at 60° to 150° for 2 - 15 minutes. Polymer departs as the first liquid evaporates and pores form therein as the second liquid evaporates from the deposit. The anchored layer produced repels liquid water but allows passage of water vapour.</p>			

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PROTECTIVE SURFACE TREATMENT

This invention relates to the treatment of substrates to prevent or at least greatly diminish the penetration into or through the substrate of liquid water while still permitting the passage into or through the substrate of water vapour.

The invention may be embodied as a method of treatment of the treated substrate itself, whether separate and capable of further fabrication into a final product or whether part of a permanent structure.

While the invention can be applied, for example, to the treatment of fabrics or the treatment of vapour-permeable layers such as natural or synthetic leather layers it can also therefore be applied to the treatment of a structural or decorative surface which needs to be permeable to water vapour while repelling or deterring the ingress of liquid water. In other words, the invention can be applied to the water-proofing of fabrics, to the surface treatment of leather, and to the surface treatment of walls, floors and ceilings to

confer water repellency.

For ease of description the invention will be discussed primarily in terms of treatment of fabrics to confer water repellency.

It is well known to provide in apparel as a protective layer against rain, or against water droplets in the form of mist, an impermeable layer of polymer or the like. While suitable for short term wear, completely impermeable articles eventually generate considerable discomfort for the user, since the inevitable water vapour generated from the skin of the user cannot escape, accumulates at the inside of the impermeable layer and condenses. The garment becomes humid and uncomfortable to wear and becomes wet inside.

Because of this it is commonplace to treat fabrics to permit more or less passage of water vapour while preventing, or hindering, passage of water droplets. The water vapour molecule is many orders of magnitude smaller than a water droplet, and can pass through fine orifices which surface tension does not allow a water droplet to penetrate.

One known method of providing a "breathable" but water-repellent fabric is to utilize a fabric the

threads of which expand upon contact with water. In normal use, the interstices between the weave are open enough to present no barrier to the passage of water vapour. If, however, the fabric is contacted with water the individual threads swell and tend to close off the gaps between them. There is still some facility for passing water vapour through such fabrics but the swollen moist fabric then prevents substantial transfer of water as liquid through from the outside to the inside.

There are, however, obvious disadvantages with such fabrics since they do become wet in use. Efficiency is not high, either for vapour transmission outwards or for the prevention of water travelling inwards.

A considerable improvement upon such materials can be obtained by conventional waterproofing, providing a water repellent coating for the fibres. This is the basis of the majority of waterproof materials, and involves treating the fabric in a solution of a water repellent polymer, typically a natural or synthetic rubber, so that a coating of such rubber is formed over each yarn or fibre. To some extent this has the effect of decreasing the size of the interstices between the fibres, but still leaving orifices through which water vapour can move inwards and outwards. However, the

water repellent nature of the coating, defining the limits of these small interstices ensures that droplets of water do not penetrate the material (unless in extreme conditions). Water is therefore deflected while preserving the inside of the garment in a dry state. The differences between this and the foregoing proposal are that the threads themselves do not become wet and swollen, and that water is turned away from the fabric by the water-repellent coating on the threads.

A further improvement in fabric characteristics can be obtained by a process involving a different type of water-repellent polymer. If a film of polytetrafluoroethylene is produced e.g. by extrusion or casting, and thereafter stretched, it breaks up as an irregular network of fibrils while still retaining its essential nature as a sheet. Instead of stretching and tearing, it undergoes innumerable small fractures and cracks. It is known to take a sheet of such fibrillated or fractured film and to sandwich it between two layers of fabric, or possibly to adhere it only to a back of the fabric layer. Such a sandwich, or such a two-layer composition, is water repellent by virtue of the high water repellency of the PTFE. Water droplets, whether as rain or mist, are far too large to penetrate the small orifices between the fibrillated material, but of course these orifices, although

small, present no barrier to the outward passage of water vapour molecules. Moreover, the fabric is free from any rubbery texture or smell, and the material has the advantage that it can be made up as a laminate from suitable reels of fabric and film, without the necessity for a dipping and curing process.

The present invention represents a new category of process for conferring water repellence upon a fabric, while retaining vapour transmitting properties. It involves both the use of a water-repellent polymer, (such as a fluoropolymer) and the use of a dipping process, and gives a product where such polymer is present in a different physical state from anything envisaged or attainable by the prior art.

It is known in a totally different technical field to provide a non-stick coating upon for example a cooking utensil by sintering to the utensil PTFE powder previously applied as a suspension to the article and dried to a layer. It is also known, as an improvement or variant of this sintering process to provide a specialised curable paint vehicle containing particles of fluoropolymer with non-stick properties, and adhering this to a surface by curing the paint rather than by sintering the particles. In each instance, however, the objective is to obtain a good

coating of material free from voids which can of course alter the non-stick properties and serve as sites for initiation of break up of the film. To this end, the surfaces to be treated are themselves typically quite smooth prior to application, so as to form a suitable basis for any provision of a non-stick sintered or cured layer.

The present invention involves the treatment of fabric with particulate water-repellent polymer and the conversion of such particulate material into an adherent and coherent polymer layer by heat treatment, the polymer layer comprising a multiplicity of voids or orifices permitting the passage of water vapour and not permitting the passage of liquid water.

By contrast therefore, whereas the prior art was concerned with taking a prepared surface and providing thereupon a good integral layer free from voids, the present invention is concerned with taking an irregular substrate such as a fabric and providing in and upon the fibres of the fabric a coherent layer but of an "imperfect" i.e. perforate nature.

In one aspect the invention describes a fabric having supported thereon and disseminated throughout at least a surface thickness of the structure thereof a

layer of water-repellent polymer including a multiplicity of orifices. A wide range of fabrics can be used; a close woven nylon fabric of 80-140g.s.m. is a typical example.

The material of the present invention is to be distinguished from known materials in which a separate layer is attached to the fabric. While this layer is supported by the fabric, it is not disseminated throughout the structure but merely exists as a separate backing or sandwiched layer.

In another aspect the invention relates to garments, more especially garments having requirements of water repellency and vapour permeability, consisting at least in part of the fabric as defined above.

The invention also provides a layer of flexible porous material (such as artificial or natural leather) having at and within a surface thickness thereof a coherent but perforate layer of a water-repellent polymer.

The invention further envisages building structure the surface of which has coated thereupon a perforate layer of polymer material closely following the pores and irregularities of the surface whereby liquid water

cannot penetrate into or through the wall but water vapour can pass outwards through the said layer.

In one aspect the invention consists in a method of providing a water-repellent but water-vapour-permeable coating over a void-containing substrate, comprising the steps of taking a solution of a fluoropolymer in a mixture comprising at least a first organic liquid which is solvent thereof and a second organic liquid non-solvent for the fluoropolymer and of lower volatility present in an amount such that no fluoropolymer is precipitated; applying the solution to at least one surface of the said substrate; and heating the substrate to drive off the mixture of liquids as vapour, whereby initial loss of first (solvent) organic liquid(s) as vapour causes fluoropolymer to deposit within the voids of the substrate and over the surface thereof and subsequent loss of second (non-solvent) organic liquid(s) as vapour causes at least in part formation of pores through the deposited surface layer.

The void-containing substrate may be solid structural or cladding material e.g. concrete, brick, plaster, masonry, chipboard, hardboard, paperboard, or composite board, having a porous nature such as to absorb liquid water into its surface and eventually transmit liquid water through its thickness. The

discontinuities or voids may be inherent or imparted as part of the production process. Alternatively, the substrate can be a protective layer to furnishing or apparel, e.g. of natural or synthetic leather, or of a foamed polymer or rubber base, as used in upholstery, camping equipment, motorvehicles, boots, shoes, gloves etc. In particular it may be a fabric, either a heavy-duty canvas or sheeting material (e.g. for camping, military or transport use) or a lighter wearable fabric as used for rainproof or shower-proof garments. The voids or discontinuities in such instances are the gaps between the warp and weft yarns (or in the knitted fabrics) and the gaps between individual fibres of which the yarns are composed.

Fabric coating is a major aspect of the invention, and a typical product comprises the original fabric within the various gaps or discontinuities of which is located a porous anchoring material of the fluoropolymer and upon at least one surface of which, integrally connected with the matrix, is a porous surface layer of the fluoropolymer. Usually although not necessarily the matrix has larger, ragged pores or interstices and a single surface layer is present as a clearly identifiable separate layer with smaller through pores and/or interconnecting cells open to the inner and outer faces.

The fluoropolymer of the present invention are homopolymers or copolymers (including terpolymers and higher) containing a carbon chain backbone to the atoms of which are attached either fluorine or a fluorinated substituted group.

Hydrogen, or other halogen, substituents may also be present to minor extents. Fluoropolymers are well known in the chemical art, and examples include polytetrafluoroethylene (PTFE) polyhexafluoropropylene (PHFP), polyvinylidene fluoride (PVDF) and the like. Moreover, numerous fluoropolymers are sold under Trade Names such as TFB 7200, the less soluble TFB 7100 (both by Hoechst containing and TFE units, HFP units and VDF vinylidene fluoride units) KYNAR (PVDF by Pennwalt) and LUMIFLON (a fluoropolymer solution including vinyl ethers and produced by solution polymerisation by Asahi) and are distinguished by their properties rather than by a disclosure of detected chemical composition.

The first organic liquid(s) can be any which is solvent for the fluoropolymer or can indeed (as in the case of LUMIFLON) be the liquid solvent of the solution as purchased i.e. xylene. It should be of higher volatility than the second liquid i.e. lower boiling point. Typically low-boiling solvents which may be used include di-aliphatic ketones (especially those ketones wherein

neither alkyl-group exceeds six carbon atoms, a preferred example being methyl isobutyl ketone, MIBK), di-aromatic ketones of similarly low molecular weights and boiling points, alkylaromatic ketones, or formamides such as dimethylformamide or pyrrolidones. The amounts of such solvents which may be used are variable depending on the starting polymer and other components, and properties desired for the coating. In general, the amount of polymer present in the solution with the first liquid, on a dry weight basis will range from say 5% to 50%, less being wasteful of solvent and of drying energy, and more giving difficulties in solution and application. More usually, from 15% to 30% of polymer is present relative to the total of the first liquid(s) and polymers.

The second, i.e. non-solvent, organic liquid(s) must be compatible with the first liquid(s), at least up to a reasonably high level of incorporation and must be less volatile e.g. have a higher boiling point. There appears to be two classes of such liquids particularly suitable for use, and especially when the first liquid is a ketone, namely (a) higher-boiling aliphatic or aromatic hydrocarbons, or mixtures thereof e.g. from C_8 , or more especially C_{12} , and above or (b) hydroxy-substituted aliphatic hydrocarbons, possibly higher alcohols such as decanols, but more especially glycols such as ethylene glycol, and the lower liquid,

polyethylene glycols e.g. up to PEG 400.

The amount of such second organic liquid(s) to be used is, in the practice of this invention, widely variable. It should not normally be so much as to precipitate the fluoropolymer before the mixture is contacted with the substrate. There should, however, be enough that the fluorocarbon will precipitate out as the coating is heated and that the vapour will at least assist in producing the necessary porosity at the surface. In general, from 1% to 50% w/w (of second liquid(s) to original solution) is used, more preferably 5% to 20%.

The man skilled in the chemical art will realise that more than one procedure is available for making up the initial solution in the mixture of liquids. The preferred procedure is to make up a solution in the said first liquid, and thereafter add the second liquid in an amount insufficient to bring about precipitation in the liquid phase.

In the practice of the invention it is preferred to heat the substrate to a temperature between 60° and 150°, and more usually between 75° and 120°C. Depending to some extent on the temperature and solvents used, from 2 to 15 minutes will generally suffice to drive off both liquids as vapour; enough time should be

allowed for escape of the second , less volatile, liquid both the upper limit does not appear to be particularly sensitive. That is to say, the deposit, once formed, appears generally stable to further temperature exposure. In most instances from 3 to 10 minutes is adequate for drying off of solvents.

Another aspect of the invention consists in a fabric substrate carrying as a protective layer against passage of liquid water the integral combination of a porous anchoring matrix of fluoropolymer located between the filaments of, and within the gaps between, the fabric yarn and a porous surface layer over at least one surface. The invention extends to such fabric in the piece or made up as weatherproof articles whether of apparel e.g. raincoats, clocks, gloves, leggings or other use e.g. tents, covers of the like.

The mechanism of the process of the invention is not fully elucidated, and may indeed partake of different features with different starting materials and operating conditions. Thus, drying-off of the second liquid(s) may merely lead to precipitation of fluoro-carbon particles, which agglomerate with void-formation upon subsequent heating (i.e. rather as an imperfect sintered coating on a solid substrate). It seems more likely, however, that some gelification or softening of the precipitate is

present, so that the agglomeration takes place before heating, and vapours are driven off and through the precipitated material to provide the necessary pores. Indeed, some formulations may tend towards uniform film-formation, all of the porosity being induced by vapour escape at different stages of coating formation. Thus, with fabric coating, it may be advantageous to at least partially seal off one face (e.g. on a process roller) during at least part of the heat treatment, to modify pore formation. However, any theory as to operation should not affect the scope of the claims appended hereto.

A particular embodiment of the invention is now described below by way of example only, and with reference to the single figure of accompanying drawing showing a diagrammatic side view of coating equipment.

EXAMPLE

20 gms of the fluoropolymer TFB 7200, supplied by Hoechst Chemicals are dissolved in 80 gms of methyl iso-butyl ketone (MIBK) to give a theoretical solids content of 20%. Once completely dissolved by high speed mixing the solution is stored in a sealed container for 4 hours to allow for de-aeration.

This solution when free from air bubbles has a

viscosity of 260 secs DIN 4 cup at 20°C.

To 20 gms of this solution between 0.5 and 2.0 gms (typically 1.0 gm) of liquid paraffin are carefully added with vigorous stirring to prevent premature precipitation of the TEB fluoropolymer. To this solution between 2.5 grms of monethylene glycol, is added, again with constant agitation. This solution is sealed, and stored for 4 hours prior to use, to enable de-aeration to take place. After this period, a typical viscosity would be 200 seconds DIN 4 at 20°C.

For laboratory purposes, a sample of a close woven nylon cloth of 120 g.s.m. is stretched between in a holding jig in the manner shown in Figure 1. It is important that the cloth is free from grease and aerial contamination, and this is achieved if severe by a commercial "genklene" wash, followed by a thorough air purge using dry air at 10 psi pressure.

Depending on the cloth density, deposition of the wet film is by K-hand coater bars (RK Print-Coat Instruments Ltd., Royston, Herts) using the 100 μ bar No. 8. It is necessary to draw down an even coating onto the cloth to prevent the formation of air bubbles. The coated sample is immediately placed into an oven having an air temperature of 110°C, for 3 minutes.

The dry coating weight was 28 g.s.m. The pressure required to force water through the cloth was greater than 15 p.s.i. The evaporation loss through the film at 36°C into an atmosphere at 18°C and 30% humidity, over 24 hours was about 3000 g per sq. metre of fabric.

Figure 1 shows a side view of suitable coating equipment is used for the above example. Fabric 2 is tensioned by clamps 2, 3 at the upper face of a holding jig 4. The K-coated bar 5 is drawn over the fabric surface in the direction of arrow A. The wet coating material 6 is thus spread uniformly over the fabric 1.

The above example can be modified and the component proportions which can be used, or characteristics achieved, can vary over a range of values. For example, from 0.5 to 5 g. of the glycol may be used, and the viscosity achieved can range from 150 to 300 seconds DIN 4 at 20°C. Fabrics of 80 - 140 g.s.m. weight have been coated, and an 80 μ coating bar has also been used. The oven temperature has been varied between 85°C and 190°C, and the time residence from 30 seconds to 5 minutes. A useful range of dry coating weight is from 25 to 40 g.s.m, and the evaporation loss can range from 2800 to 4000 g/m²/24 hours under the conditions specified above.

EXAMPLE 2

20 grms of fluoropolymer TFB 7200 supplied by Hoechst Chemicals are dissolved in 80 grams of methyl isobutyl ketone (MIBK) to give a theoretical solids content of 20%. Once completely dissolved by high speed mixing the solution is stored in a sealed container for 6 hours to allow for de-aeration.

This solution when free from air bubbles has a viscosity of 269 secs DIN4 cup at 20°C.

To 100 grms of this solution between 10 grms of mono ethylene glycol are carefully added with vigorous stirring.

For laboratory purposes a sample of a close woven nylon cloth of 100 gms/sq. metre is stretched in a holding jig in the manner shown in Fig. 1. It is important that the cloth is free from grease and aerial contamination.

Depending on cloth density deposition of the wet film is by K-hand coater bars, selecting the correct bar to give a dry coating weight of between 20 and 25 g.s.m. The coated sample is immediately placed in an oven at an air temperature of 80°C for 5 minutes. At this coating

weight the pressure required to force water through the cloth was 15 psi.

The evaporation rate through the film 24°C into an atmosphere at 18°C and between 50 and 60% relative humidity over 24 hours was of the order of 2500 g per sq. metre of fabric.

EXAMPLE 3.

20 grms of PVDF (commercial name Kynar, supplied by Pennwalt Company Limited) was dissolved in 80 grms of dimethyl formamide and allowed to deaerate in the manner of Example 1.

To 100 grms of this solution between 8.5 grms of mono ethylene glycol was added with vigorous stirring. (Alternatively both dimethyl formamide and mono ethylene glycol can be pre-mixed and the PVDF solid slowly added again with vigorous stirring).

The cloth was then coated in a similar manner to Example 1 and immediately placed in an oven at an air temperature of 150°C for 5 minutes. Cloth coated in this manner exhibited blow-through pressures of 20 psi whilst having an evaporation loss of 1500 grms/M²/24 hours.

EXAMPLE 4

To 100 grms of the fluoropolymer "Lumiflon" solution supplied by ICI Mond Division, 8.5 grms of mono ethylene glycol was added again with vigorous stirring.

The resulting solution after de-aeration was applied to the cloth as for example in Fig. 1 and heat treated for between 5 minutes at an air temperature of 150°C. The coated sample exhibited a blow through pressure of 35 psi with a water evaporation rate of 800 gms/m²/24 hours.

Claims.

1. A method of providing a water-repellent but water-vapour-permeable coating over a void-containing substrate, comprising the steps of taking a solution of a fluoropolymer in a mixture comprising at least a first organic liquid which is solvent thereof and a second organic liquid non-solvent for the fluoropolymer and of lower volatility present in an amount such that no fluoropolymer is precipitated; applying the solution to at least one surface of the said substrate; and heating the substrate to drive off the mixture of liquids as vapour, whereby initial loss of first (solvent) organic liquid(s) as vapour causes fluoropolymer to deposit within the voids of the substrate and over the surface thereof and subsequent loss of second (non-solvent) organic liquid(s) as vapour causes at least in part formation of pores through the deposited surface layer.

2. A method as claimed in claim 1 in which the fluoropolymer is chosen from the group consisting of TFE/HFP/VDF copolymer, a LUMIFLON and PVDF polymer.

3. A method as claimed in claim 1 in which the first organic liquid is chosen from the group consisting of dialiphatic ketones, diaromatic ketones, alkylaromatic ketones, formamides and pyrrolidones.

4. A method as claimed in claim 3 in which the amount of polymer present in relation to the first liquid(s) is from 5 to 50% w/w.

5. A method as claimed in claim 1 in which the second organic liquid(s) is chosen from the group consisting of higher-boiling-point aliphatic and aromatic hydrocarbons, hydroxy-substituted higher aliphatic hydrocarbons, glycols and polyethylene glycols.

6. A method as claimed in claim 1 in which the second organic liquid(s) is present in an amount of from 1 to 50% w/w of the solution of polymer in the first organic liquid.

7. A method as claimed in claim 1 in which the liquid applied to the substrate is made up by (a) dissolving the polymer in the first organic liquid(s) and thereafter (b) adding the second organic liquid(s).

8. A method as claimed in claim 1 in which the substrate is heated to a temperature between 60° and 150 °C for a period between 2 and 15 minutes.

9. A method as claimed in any one of claims 1 to 8 applied to a solid structural or cladding material.

10. A method as claimed in any one of claims 1 to 8 applied to a protective leather-like or rubbery material.

11. A method as claimed in any one of claims 1 to 8 applied to a fabric.

12. A method as claimed in any one of claims 1 to 8 applied to a made-up garment.

13. A fabric substrate carrying as a protective layer against passage of liquid water the integral combination of a porous anchoring matrix of fluoropolymer located between the filaments of, and within the gaps between, the fabric yarn and a porous surface layer over at least one surface.

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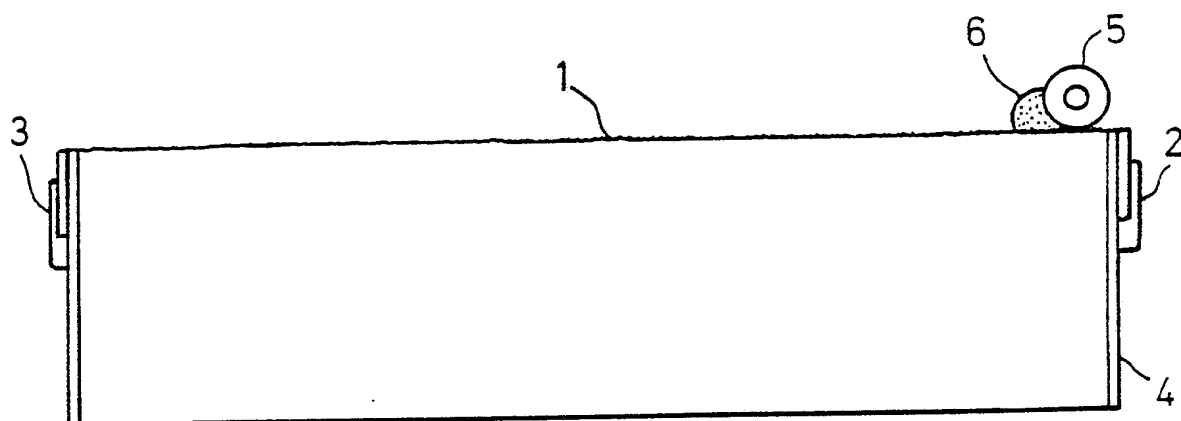


FIG. 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 88/00117

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : D 06 M 15/256; D 06 N 3/04; C 08 J 9/28																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px; vertical-align: top;">IPC⁴</td> <td style="padding: 5px; vertical-align: top;">D 06 N; D 06 M; C 08 J; C 09 D; C 09 K; D 21 H; A 41 D</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁴	D 06 N; D 06 M; C 08 J; C 09 D; C 09 K; D 21 H; A 41 D											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category ⁹</th> <th style="border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 15%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top;">X,Y</td> <td style="padding: 5px; vertical-align: top;">DE, A, 2632185 (SUMITOMO ELECTRIC INDUSTRIES) 27 January 1977 see the whole document --</td> <td style="text-align: center; vertical-align: top;">1-7,10-13</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top;">Y</td> <td style="padding: 5px; vertical-align: top;">GB, A, 981642 (E.I. DU PONT DE NEMOURS) 27 January 1965 see page 3, lines 57-80; page 4, lines 28-105; claims 1-16 --</td> <td style="text-align: center; vertical-align: top;">1-7,10-13</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="padding: 5px; vertical-align: top;">GB, A, 2040293 (SKW TROSTBERG) 28 August 1980 see claims --</td> <td style="text-align: center; vertical-align: top;">1,3,9,10</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="padding: 5px; vertical-align: top;">GB, A, 2122630 (ASAHI GLASS) 18 January 1984 see example 1; claims 1-3,7 -----</td> <td style="text-align: center; vertical-align: top;">1-6,9</td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X,Y	DE, A, 2632185 (SUMITOMO ELECTRIC INDUSTRIES) 27 January 1977 see the whole document --	1-7,10-13	Y	GB, A, 981642 (E.I. DU PONT DE NEMOURS) 27 January 1965 see page 3, lines 57-80; page 4, lines 28-105; claims 1-16 --	1-7,10-13	A	GB, A, 2040293 (SKW TROSTBERG) 28 August 1980 see claims --	1,3,9,10	A	GB, A, 2122630 (ASAHI GLASS) 18 January 1984 see example 1; claims 1-3,7 -----	1-6,9
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A	GB, A, 2040293 (SKW TROSTBERG) 28 August 1980 see claims --	1,3,9,10															
A	GB, A, 2122630 (ASAHI GLASS) 18 January 1984 see example 1; claims 1-3,7 -----	1-6,9															
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">20th May 1988</td> <td style="border-bottom: 1px solid black; padding: 5px; text-align: right;">21 JUN 1988</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">International Searching Authority</td> <td style="border-bottom: 1px solid black; padding: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="padding: 5px;">EUROPEAN PATENT OFFICE</td> <td style="padding: 5px; text-align: right;"> P.C.G. VAN DER PUTTEN </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	20th May 1988	21 JUN 1988	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	 P.C.G. VAN DER PUTTEN							
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International Searching Authority	Signature of Authorized Officer																
EUROPEAN PATENT OFFICE	 P.C.G. VAN DER PUTTEN																

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 8800117

SA 20929

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 09/06/88
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A- 2632185	27-01-77	FR-A, B 2333825	01-07-77
		GB-A- 1552942	19-09-79
		JP-A- 52011261	28-01-77
		CA-A- 1068458	24-12-79
		US-A- 4238571	09-12-80
		JP-A- 52154862	22-12-77
GB-A- 981642		DE-A- 1444165	17-10-68
		LU-A- 42888	18-02-63
		US-A- 3208875	
		CH-A- 446263	
		BE-A- 626816	
		FR-A- 1355577	
GB-A- 2040293	28-08-80	NL-A- 287476	
		BE-A- 881228	16-05-80
		FR-A, B 2446854	14-08-80
		DE-A, C 2902095	24-07-80
		SE-A- 8000420	20-07-80
		US-A- 4416925	22-11-83
GB-A- 2122630	18-01-84	CH-A- 643877	29-06-84
		SE-B- 447907	22-12-86
		DE-A- 3323271	29-12-83
		JP-A- 59004473	11-01-84
		US-A- 4503097	05-03-85